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STRUCTURE AND PROPERTIES OF NANOPOROUS CERAMIC Al_2O_3 OBTAINED BY ISOSTATIC PRESSING

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Nanoporous ceramic with pore volume of the order of 60% is obtained from nanosize Al_2O_3 powder by isostatic pressing. The microstructure, porosity and strength of the ceramic obtained are studied. Technological conditions for obtaining nanoporous ceramic which secure the optimal combination of strength and porosity are determined.

Key words: ceramic, aluminum oxide, cold isostatic pressing, nanostructure, porosity.

High-porosity ceramic materials obtained from pure high-refractory oxides (Al_2O_3, BeO, ZrO_2, MgO and others) possess a number of valuable properties aside from high heat-resistance (> 2000°C): chemical inertness, low electric conductivity, high resistance to corrosion and so forth. This makes it possible to use such materials very effectively under different operating conditions. However, the main problem at present is that as porosity and pore size increase the strength of ceramic materials obtained by conventional technologies decreases sharply [1].

The use of nanopowders and adequate methods of molding and sintering them will increase the mechanical characteristics of porous ceramic materials owing to the fine micron-scale microstructure, which will make it possible to produce parts and articles with many-fold longer service life and expand the range of applications. Specifically, a nanostructure ceramic based on aluminum oxide can be especially promising owing to the long service life and considerable room for improving the mechanical properties by transitioning into a nanostructural state.

The method used to obtain porous materials has a large effect on the character of the formation of the porous structure of materials. In addition, the total porosity and the character of the structure of the porous material can be regulated by changing the technological parameters used for the production of articles (mainly at the molding stage).

At the present time porous ceramic materials are produced mainly by following means [2]: the introduction of a burnable additive with low ash content; addition of foaming agents or separately prepared foam to suspensions of ceramic material; gas-formation using chemical reactions; microspheres of high-refractory oxides obtained by plasma treatment of powders.

The burnable additive method makes it possible to obtain materials with porosity to 50 – 60% [3] and low through porosity.

The highest porosity up to 85 – 90% is attained only by using gaseous methods. However, ceramic obtained by this method has 90% closed porosity.

The method of obtaining a porous ceramic from microspheres of highly refractory oxides has significant limitations due to, first and foremost, the impossibility of obtaining microspheres of submicron size. The minimal size of microspheres in such materials is 20 ìm; the volume porosity reaches 30 – 40% [4].

The loose packing of ungranulated nanosize powders makes it possible to obtain porous ceramic with a high percentage content of through porosity in submicro- and nanosize ranges. The problem lies in securing a uniform density distribution of dust-like nanopowders in compacts and preserving the nanostructure in pressings for forming nanosize grains during sintering, i.e., it is necessary to create conditions for suppressing grain growth and for sintering high-quality nanoceramic articles with prescribed functional properties. These problems can be solved to a certain extent by using the cold isostatic pressing method, which secures uniform particle packing in pressings and does not require any binder for compacting nanosize powders [5].

The aim of the present work is to obtain by isostatic pressing a wide range of nanoporous ceramic materials for technical applications with a uniform volume distribution of submicron and nanosize pores.

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EXPERIMENTAL MATERIALS AND PROCEDURE

γ-Al_2O_3 nanopowder was used to obtain nanoporous ceramic. The nanopowder, pre-kilned at 900°C for 1 h, was placed into a flexible rubber mold and compacted on a vibrating table. Next, the samples of nanosize ceramic were compacted by cold isostatic pressing at 18°C and pressure from 5 to 50 MPa, after which the pressure was reduced to atmospheric pressure and the samples were removed from the rubber mold. The compacted samples were sintered at 1300, 1400 and 1500°C for 2 h in air. The sintered samples were hand ground in order to impart the correct shape.

The morphology of the particles of the initial aluminum oxide nanopowder was studied by means of transmission electron microscopy (TEM).

A TriStar 3020 specific surface area analyzer was used to measure the specific surface area.

Scanning electron microscopy (SEM) was used to investigate on chips the microstructure of nanoporous ceramic samples.

The volume and pycnometric density of sintered nanoporous ceramic samples were determined by weighing and helium pycnometry. The average density of relative to the x-ray density of α-Al_2O_3 was calculated using the relation

$$P = (\rho_{theor} - \rho_{exp})/\rho_{theor} \times 100\%, \quad (1)$$

where P is the porosity, %; ρ_{theor} is the theoretical density, kg/m^3; and, ρ_{exp} is the experimental density, kg/m^3.

Mercury porometry (AutoPOre IV 9500) was used to study the pore-size distribution. The BET method (TriStar 3020 specific surface area analyzer) was used to determine the total surface area of the pores.

The ultimate strength to rupture of the nanoporous ceramic obtained was determined by the standard procedure using the INSTRON 5882 universal, electromechanical, floor, testing machine.

RESULTS AND DISCUSSION

The morphological characteristics and structuredness of powders and the size and density of the particles and aggregates determine the sintering process in ceramics, including the formation of green parts, conventionally understood as the first stage of sintering [3].

Scanning electron microscopy (SEM) established that after heat-treatment at 900°C the nanosize Al_2O_3 powder consists of spherical particles with average size 10 – 50 nm (Fig. 1). The BET specific surface area of the powder after kilning was 98.9173 m^2/g.

The production of nanoporous ceramic in the present work is based on the assertion that the mechanical properties of ceramic, including ceramic based on Al_2O_3, can be increased dramatically by creating a material with a fine uniform structure [6].

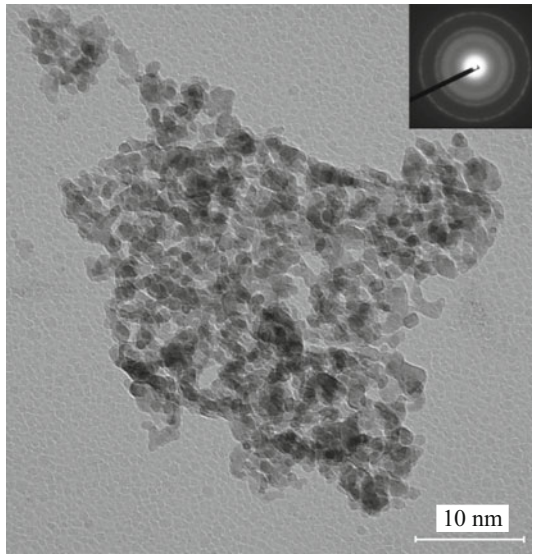

Fig. 1. SEM image of an agglomerate of Al_2O_3 power after heat-treatment at 900°C.

The decrease of strength with increasing porosity is explained by a decrease of the "working" cross section of a porous body and the contact surfaces of grains and stress concentration in the weakened cross sections. For this reason, to assess the strength of porous materials their structure must be taken into account together with the porosity.

Scanning electron microscopy (SEM) studies of the fracture surfaces of ceramic obtained from nanosize Al_2O_3 powder established that the experimental samples have a formed grain structure with grain size ranging from 100 to 600 nm (Fig. 2). The material obtained possesses a high-porosity framework with an extended system of channel-forming pores.

An advantage of such a microstructure for a ceramic to be used in technical applications is a considerable increase in the surface area of intercrystallite boundaries and the number of their triple junctions owing to the development of a relief.

It is known that when ceramic refractory parts are pressed from disperse solid particles the parts with the highest porosity are those which were made using mixtures with spherical grains which are all of the same size. In the technology of refractories it is necessary to deal with grains of different sizes and nonspherical shapes. Nonetheless, the porosity of a real particle packing is quite high. It is not possible to retain the high porosity in parts, since pressing results in densification, which is all the greater, the higher the pressing pressure is. For this reason efforts are made to press porous mixes under a low specific pressure. At elevated pressure not only do particle agglomerates are brought closer to one another but they undergo deformation and are crushed and therefore the density of the parts obtained increases [2].

In summary, these studies established that as the pressing pressure increases above 8 MPa the nanoporous ceramic material is more compacted; at pressure less than 8 MPa the

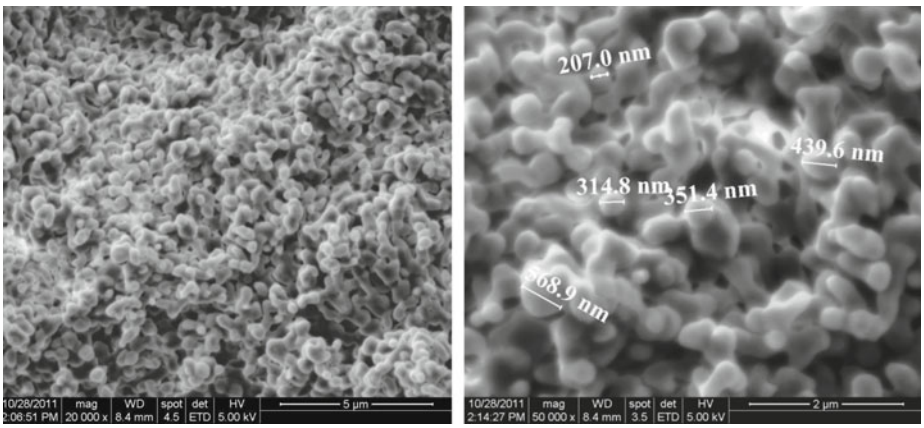

Fig. 2. SEM image of a chip surface of samples of Al_2O_3 porous ceramic after kilning at 1400°C.

powder compacts partially while the optimal combination of strength and porosity of a green compact is reached at pressing pressure 8 MPa and holding time 1 min.

Conventionally, ceramic materials are sintered using regimes determined in accordance with the known phase diagrams, which, as a rule, are constructed using data from analysis of solid-phase reactions.

The use of nanosize powder initially to obtain ceramic made it possible to intensify considerably the effect of their sintering by increasing the contact zones of powders and the diffusion coefficient gradient, which accelerates mass transfer considerably, as a result of which the material undergoes compaction [7].

The sintering regime for nanoporous ceramic was found experimentally. The samples were sintered at 1300, 1400 and 1500°C. The optimal combination of porosity and strength was obtained for samples sintered at 1400°C.

The effect of porosity on the properties of solids is recognized and a subject of numerous studies because of the great scientific and technical interest in this question [8]. Even a single (isolated) pore in a sample is capable of sharply lowering rupture strength because of stress concentration on the boundaries of the pore, especially if the pore is wedge-shaped, which in this case is called a crack. However, saturation of the interior of a body by an ensemble of pores, characterized by the concept of porosity (the volume fraction of the body that is occupied by pores), increases the effect of pores on strength. The structural characteristics of porous materials are: general, or true, porosity; closed porosity; open, or apparent, porosity; pore size and pore size ratio; permeability; average pore diameter; specific surface area of pores; permeability. For all porous materials the most important characteristics are the size and shape of the pores.

The average porosity of the experimental samples was 60%. The pycnometric density of porous sintered samples is ≥ 3.9 g/cm^3, which is 97% of the x-ray density of α-Al_2O_3. Thus, the porosity obtained in experimental samples is permeable, while the isolated porosity does not exceed 3%. The pore-size distribution in the experimental samples is presented in Fig. 3.

Mercury porometry shows that porosity 26.4% and average pore diameter 616.7 nm. Since the lower measurement limit of the mercury porosimeter is 360 nm (Fig. 3), in the porous ceramic samples obtained the diameter of at least 50% of the pores is less than 360 nm, while the average diameter of the pores is much shorter.

The total BET surface area of the pores in the ceramic samples was 1.68 m^2/g.

The strength of porous refractory materials was determined according to the ultimate compression strength. Studies of the mechanical properties of ceramics were performed on 15 × 10 × 10 mm samples sintered at 1400°C. The

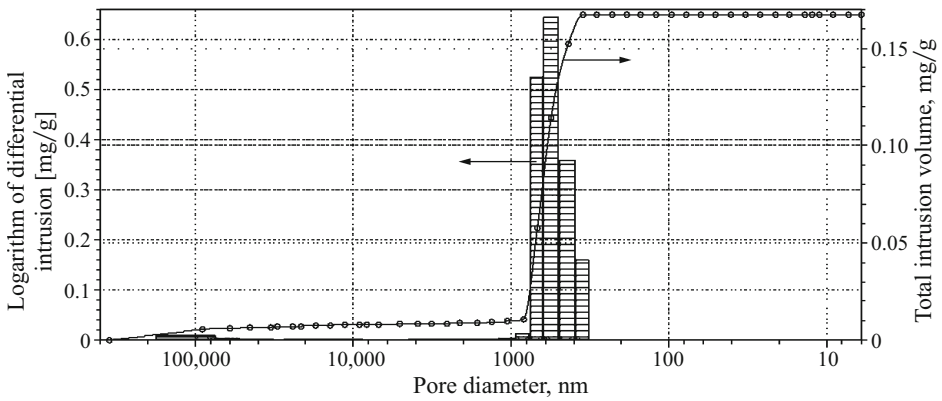

Fig. 3. Pore size distribution in porous Al_2O_3 ceramic samples after kilning at 1400°C.

tests were performed with a constant rate of loading; the axial compression load and deformation of the samples were recorded. The ultimate compression strength of the experimental samples was 50 MPa, which corresponds to the porosity – ultimate compression strength characteristics of porous ceramic produced in Russia.

CONCLUSIONS

It was determined that the pore structure of nonporous ceramic material obtained from nanosize Al_2O_3 powder comprises a system of continuous channel-forming pores of disordered shape. Actually, such a structure corresponds to two interpenetrating components: a ceramic framework and a communicating pore space.

The porous structure of the ceramic obtained is characterized by a unimodal pore-size distribution, average pore size 616.7 nm, uniform distribution of pores over the volume, permeable porosity of the order of 60% and isolated porosity no greater than 3%.

In summary, mechanically strong nanoporous ceramic Al_2O_3 (ultimate compression strength 50 MPa), obtained by isostatic pressing from nanosize aluminum oxide powder, holds great promise for different practical applications.

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